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Densities and viscosities of imidazolium and pyridinium chloroaluminate ionic liquids

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ABSTRACT

The chloroaluminate ionic liquids are used in various types of reactions. However, due to their particular vulnerability on water, their physical properties have not been previously investigated very extensively. The densities and viscosities of series imidazolium and pyridinium chloroaluminate ionic liquids having alkyl (butyl, hexyl, octyl) or aralkyl (benzyl, ethylphenyl) chain at the cation, various effective molar fraction of AlCl₃ ($\chi_{AlCl3} = 0.5$, 0.65, 0.7), as well as they mixture and mixture with common organic solvents (hexane, toluene) were measured at the temperature range 293.15–343.15 K (20–70 °C). Densities, and particularly viscosities decrease with the increase of temperature. The density decreases with the increase of the length of the alkyl chain. The type of cation also influences the density, however, the order is different than for non-haloaluminate ionic liquids and depends on the alkyl chain length. Viscosity increases with increasing alkyl chain length, but it is not a linear trend. The ionic liquid with meta position of the alkyl chain is considerably more dense and more viscous than para isomer. The presence of aromatic phenyl ring at the side chain of the cation increases both density and viscosity. Higher effective molar fraction of AlCl₃ increases density and decreases viscosity, however, for the imidazolium ionic liquid the change of viscosity diminishes at higher temperatures. Organic solvents decrease both density and viscosity of the ionic liquids, but aliphatic hexane imposes much smaller effect than aromatic toluene. The mixture of two ionic liquids has density and viscosity between those for constituents. This extends the application of the aralkyl ionic liquids over temperatures, in which they are in solid state.

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1. Introduction

lonic liquids are commonly defined as organic salts in the liquid state below 100 °C (373.15 K). They are usually consisted of bulky, asymmetric, organic cation and organic/inorganic anion [1–4]. They attract a considerable interest because of their useful properties: high polarity, very low volatility, inflammability, thermal, chemical, and electrochemical stability, ability to dissolve many organic, inorganic, and organometallic compounds, and modulated miscibility with many organic solvents [2,5–7]. An unique feature of the ionic liquids is the possibility to control their physical and chemical properties, such us viscosity, density, surface tension, and acidity, through the choice of cation/anion combination or through the introduction of special functional groups into the structure of cation or anion [2,7–14].

The research areas on the ionic liquids are growing very rapidly, and their application is expanding into numerous application fields. The ionic liquids was found to be useful, for example: as electrolytes in electrochemistry, as solvents in chemical synthesis and catalysis, in liquid-liquid extractions, in gas–liquid absorption, in liquid membrane separations, in nanomaterial technologies, as stationary phases for chromatography, as supports for the immobilization of enzymes, as antimicrobial agents, as lubricants, and plasticizers [4,7,15–26].

One of the most known types of the ionic liquids are chloroaluminates, called the first generation ionic liquids. They are synthesized from AlCl₃ and proper organic chloride salts. It enables to control Lewis acidity of the chloroaluminate ionic liquids, by the molar ratio of AlCl₃ to organic chloride (so called the effective molar fraction of AlCl₃, χ). If the AlCl₃ mole fraction (χ) equals 0.5, generally AlCl₄ anions are created and the obtained ionic liquid is neutral. Lewis basic ionic liquid can be obtained at χ <0.5, where Cl⁻ and AlCl₄ anions are present and Lewis acidic systems can be obtained at χ >0.5, where Al₂Cl₇ and Al₃Cl₁₀ anions exist [12,13,15,27].

In early stage, the studies into the chloroaluminate ionic liquids concerned their application as electrochemical solvents [15,28,29]. Presently, they are popular medium applied in many types of organic reactions such as: Friedel–Crafts, Diels–Adler, hydrogenation, Knoevenagel condensation, Pechman condensation, catalytic cracking of polyethylene as well as olefins dimerization, isomerization, oligomerization, and polymerization. In many cases, application of the ionic liquids improves yield and/or selectivity of the reaction, enables to separate product easily and re-use catalytic systems, what is particularly valuable in the case of reactions performed using transition metal compounds [27,30–48].

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Main disadvantage of the chloroaluminate ionic liquids is high vulnerability on impurities, particularly water (even in form of humidity), which has considerable impact on their physical and chemical properties. Therefore, special reaction conditions must be preserved during the synthesis, characteristic, and application of the chloroaluminates. In laboratory scale, all operations require atmosphere of an inert gas as well as glove-box and Schlenk technique [49]. These difficulties result in limited number of literature data concerning physical characteristic of the chloroaluminate ionic liquids [50,51]. However, the basic physical properties, such as density or viscosity, can have profound influence on the performance of the reaction carried out in the ionic liquid medium i.e.; mass transfer, diffusion of substrates and products, separation of immiscible phases, accessibility of the active centers, pumping cost, adhesion to apparatuses.

In the present research we measured the viscosities and densities of twelve chloroaluminate ionic liquids. Commonly applied imidazolium and pyridinium cations have been chosen. The effect of the substituent at the ionic liquid cation, temperature in the range (293.15–343.15 K),

Table 1

The studied ionic liquids.

the effective molar fraction of $AlCl_3$, and two main solvent hexane and toluene were investigated (Table 1). We believe that data presented in this work will be valuable for those who apply the chloroaluminate ionic liquids, and will help to control better reaction performance by careful choosing the ionic liquid most suitable for the process.

2. Experimental

The ionic liquids based on the chloroaluminate anion are very sensitive to air moisture. Therefore, it is extremely important to handle them in atmosphere with the absence of water, as much as it is technically possible. All laboratory operations were performed in glass apparatus or glove-box flushed with a nitrogen controlled atmosphere. Our practice indicates that neutral gases (nitrogen, argon) commonly applied in laboratory are not sufficiently dry and contain small amount of water. Therefore it is extremely important to purify them before they can be used in technical operation. I this work it was performed by passing nitrogen through a column of sodium metal supported on Al₂O₃. Also, the

ID	Structure	Name	Abbreviation	Molecular formula and weight, g∙mol ⁻¹	Appearance
1		1-n-Butyl-3-methylimidazolium tetrachloroaluminate	[C ₄ -mim] [AlCl ₄]	C ₈ H ₁₅ AlCl ₄ N ₂ 308.02	Clear yellow liquid
2		1-n-Hexyl-3-methylimidazolium tetrachloroaluminate	[C ₆ -mim] [AlCl ₄]	C ₁₀ H ₁₉ AlCl ₄ N ₂ 336.07	Clear yellow liquid
3		1-n-Octyl-3-methylimidazolium tetrachloroaluminate	[C ₈ -mim] [AlCl ₄]	C ₁₂ H ₂₃ AlCl ₄ N ₂ 364.12	Clear yellow liquid
4		1-n-Butylpyridinium tetrachloroaluminate	[C ₄ -py] [AlCl ₄]	C ₉ H ₁₄ AlCl ₄ N 305.01	Clear pale green liquid
5		1-n-Hexylpyridinium tetrachloroaluminate	[C ₆ -py] [AlCl ₄]	C ₁₁ H ₁₈ AlCl ₄ N 333.07	Clear yellow liquid
6		1-n-Octylpyridinium tetrachloroaluminate	[C ₈ -py] [AlCl ₄]	C ₁₃ H ₂₂ AlCl ₄ N 361.12	Clear yellow liquid
7		1-n-Butyl-4-methylpyridinium tetrachloroaluminate	[C ₄ -4-mpy] [AlCl ₄]	C ₁₀ H ₁₆ AlCl ₄ N 319.04	Clear pale brown liquid
8		1-n-Hexyl-4-methylpyridinium tetrachloroaluminate	[C ₆ -4-mpy] [AlCl ₄]	C ₁₂ H ₂₀ AlCl ₄ N 347.09	Clear pale brown liquid
9		1-n-Octyl-4-methylpyridinium tetrachloroaluminate	[C ₈ -4-mpy] [AlCl ₄]	C ₁₄ H ₂₄ AlCl ₄ N 375.15	Clear pale brown liquid
10	AICI ₄	1-n-Octyl-3-methylpyridinium tetrachloroaluminate	[C ₈ -3-mpy] [AlCl ₄]	C ₁₄ H ₂₄ AlCl ₄ N 375.15	Clear pale brown liquid
11		1-Benzyl-3-methylimidazolium tetrachloroaluminate	[Bzl-mim] [AlCl ₄]	C ₁₁ H ₁₃ AlCl ₄ N ₂ 342.03	Clear pale brown liquid above 318.15 K (45 °C)
12		1-(2-Phenylethyl)-3-methylimidazolium tetrachloroaluminate	[Ph-C ₂ -mim] [AlCl ₄]	C ₁₂ H ₁₅ AlCl ₄ N ₂ 356.06	Clear pale brown liquid above 313.15 K (40 °C)

Table 2					
Densities	(g·cm ^{-±}	3) of the	studied	ionic	liquids.

No	Ionic liquids	T (K)														
		293.15	296.15	298.15	301.15	303.15	305.15	308.15	311.15	313.15	315.15	318.15	321.15	323.15	325.15	328.15
1	$[C_4-mim][AlCl_4]$	1.2455	1.2447	1.2435	1.2425	1.2416	1.2408	1.2397	1.2385	1.2375	1.2367	1.2357	1.2345	1.2337	1.2328	1.2317
2	$[C_6-mim][AlCl_4]$	1.1847	1.1841	1.1829	1.1820	1.1811	1.1806	1.1795	1.1784	1.1775	1.1770	1.1759	1.1750	1.1743	1.1734	1.1725
3	[C ₈ -mim][AlCl ₄]	1.1226	1.1219	1.1206	1.1192	1.1187	1.1179	1.1166	1.1156	1.1146	1.1137	1.1127	1.1116	1.1105	1.1099	1.1085
4	[C ₄ -py][AlCl ₄]	Solid	Solid	Solid	1.2771	1.2763	1.2755	1.2742	1.2731	1.2722	1.2714	1.2701	1.2689	1.2682	1.2672	1.2661
5	[C ₆ -py][AlCl ₄]	1.2159	1.2152	1.2142	1.2133	1.2128	1.2120	1.2110	1.2102	1.2095	1.2088	1.2079	1.2073	1.2064	1.2060	1.2051
6	[C ₈ -py][AlCl ₄]	1.1956	1.1948	1.1935	1.1925	1.1915	1.1907	1.1895	1.1883	1.1873	1.1862	1.1851	1.1839	1.1829	1.1819	1.1809
7	$[C_4-4-mpy][AlCl_4]$	1.2064	1.2054	1.2042	1.2030	1.2021	1.2013	1.1999	1.1989	1.1979	1.1969	1.1957	1.1946	1.1936	1.1930	1.1919
8	[C ₆ -4-mpy][AlCl ₄]	1.1462	1.1455	1.1445	1.1436	1.1430	1.1423	1.1415	1.1405	1.1399	1.1393	1.1384	1.1376	1.1369	1.1363	1.1354
9	[C ₈ -4-mpy][AlCl ₄]	1.1242	1.1233	1.1222	1.1210	1.1200	1.1193	1.1181	1.1167	1.1158	1.1149	1.1136	1.1124	1.1114	1.1104	1.1094
10	[C ₈ -3-mpy][AlCl ₄]	1.1651	1.1647	1.1635	1.1624	1.1616	1.1609	1.1598	1.1588	1.1580	1.1572	1.1564	1.1553	1.1543	1.1537	1.1526
11	[Bzl-mim][AlCl ₄]	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	1.3490	1.3486	1.3482	1.3479	1.3476	1.3472
12	[Ph-C ₂ -mim][AlCl ₄]	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	1.2588	1.2583	1.2575	1.2569	1.2564	1.2559	1.2552
13	$[C_4-mim][AlCl_4]/[Ph-C_2-mim]$	1.2554	1.2548	1.2535	1.2524	1.2517	1.2511	1.2500	1.2489	1.2481	1.2474	1.2460	1.2452	1.2444	1.2437	1.2426
	$[AlCl_4] = 1/1$															
14	$[C_4-mim][AlCl_4]/[Ph-C_2-mim]$	1.2493	1.2483	1.2471	1.2460	1.2452	1.2443	1.2430	1.2418	1.2411	1.2403	1.2391	1.2378	1.2371	1.2363	1.2352
	$[AlCl_4] = 1.5/1$															
15	[C ₄ -mim][AlCl ₄]/AlCl ₃	1.3265	1.3256	1.3243	1.3232	1.3223	1.3214	1.3202	1.3189	1.3178	1.3172	1.3158	1.3146	1.3138	1.3128	1.3114
	$\chi = 0.65$															
16	[C ₄ -mim][AlCl ₄]/AlCl ₃	1.3476	1.3468	1.3455	1.3443	1.3434	1.3425	1.3413	1.3399	1.3390	1.3382	1.3368	1.3357	1.3348	1.3338	1.3324
	$\chi = 0.7$															
17	[C ₄ -mim][AlCl ₄]/hexane	1.1445	1.1439	1.1427	1.1419	1.1411	1.1403	1.1391	1.1382	1.1373	1.1365	1.1356	1.1345	1.1337	1.1329	1.1317
18	[C ₄ -mim][AlCl ₄]/toluene	1.0660	1.0654	1.0644	1.0636	1.0627	1.0621	1.0613	1.0602	1.0594	1.0586	1.0578	1.0566	1.0560	1.0553	1.0542
19	[C ₄ -py][AlCl ₄]/AlCl ₃	1.3609	1.3598	1.3586	1.3576	1.3566	1.3559	1.3544	1.3533	1.3523	1.3514	1.3501	1.3487	1.3481	1.34/1	1.3460
20	$\chi = 0.65$	1 2027	1 2020	1 2017	1 2005	1 2707	1 2700	1 2775	1 2762	1 2752	1 2745	1 2720	1 2717	1 2700	1 2007	1 2007
20	$[C_4-py][AlCl_4]/AlCl_3$	1.3837	1.3829	1.3817	1.3805	1.3/9/	1.3788	1.3775	1.3762	1.3/52	1.3745	1.3730	1.3/1/	1.3709	1.3697	1.3087
21	$\chi = 0.7$					1 1602	1 1 6 9 4	1 1672	1 1662	1 1652	1 1644	1 1624	1 1625	1 1617	1 1607	1 1 5 0 7
21	$[C_{4}-py][AlCl_{4}]/llexalle$	-	-	-	-	1.1092	1.1084	1.10/3	1.1003	1.1003	1.1044	1.1034	1.1025	1.101/	1.1007	1.1397
22	[C4-py][AlCl4]/toluelle	1.0900	1.0970	1.0900	1.0930	1.0952	1.0944	1.0952	1.0923	1.0910	1.0909	1.0697	1.0000	1.0001	1.00/3	1.0004

(3)

solvent used during the synthesis must be stored (or freshly distilled) over the proper desiccants. The ionic liquids were stored in argon filled desiccator in glass flasks with glass stoppers covered by silicone grease for high vacuum and each flask was placed in argon filled polyethylene bag.

2.1. Materials

Pyridine- C_5H_5N (Sigma–Aldrich), 4-picoline- C_6H_7N (Aldrich), 3picoline- C_6H_7N (Fluka), 1-chlorobutane- C_4H_9Cl (Fluka), 1chlorohexane- $C_6H_{13}Cl$ (Aldrich), 1-chlorooctane (Aldrich), 1methylimidazole- $C_4H_6N_2$, (Aldrich), (2-chloroethyl)benzene- $_8H_9Cl$ (Aldrich), benzyl chloride- C_7H_7Cl (Sigma), aluminium chloride-AlCl₃ (Aldrich) were applied as purchased. Diethyl ether (C_2H_5)₂O and toluene C_7H_8 (POCH, Gliwice) were distilled over metallic sodium. Pure grade hexane (POCH, Gliwice) was refined with sulfuric acid and sodium hydroxide, distilled to gain a fraction (62–67 °C), and distilled again over sodium/benzophenone, and stored over metallic sodium. The acetonitrile-CH₃CN (POCH, Gliwice) and ethyl acetate-CH₃COOC₂H₅ (POCH, Gliwice) were stored over molecular sieves. Pure nitrogen (Polgaz) and argon (Remgaz) were used after having been passed through a column of sodium metal supported on Al₂O₃.

2.2. Ionic liquid synthesis

$$1 - n - butyl - 3 - methylimidazolium tetrachloroaluminate,$$
 (1)
[C₄ - mim][AlCl₄]

$$1 - n - hexyl - 3 - methylimidazolium tetrachloroaluminate,$$
 (2)
[C₆ - mim][AlCl₄]

$$\label{eq:constraint} \begin{array}{l} 1-n-octyl-3-methylimidazolium tetrachloroaluminate, \\ [C_8-mim][AlCl_4] \end{array}$$

The compounds were synthesized according to the procedure reported previously [47]

 $1 - n - butylpyridinium tetrachloroaluminate, ([C_4 - py][AlCl_4])$ (4)

 $1 - n - hexylpyridinium tetrachloroaluminate, ([C_6 - py][AlCl_4])$ (5)

 $1 - n - \text{octylpyridinium tetrachloroaluminate}, ([C_8 - py][AlCl_4])$ (6)

Pyridine (0.4 mol) and 1-chlorobutane (or 1-chlorohexane or 1-chlorooctane) (0.4 mol) were placed into a 250 cm³ round bottom flask equipped with an electric heat-jacket and vigorously stirred using a magnetic stirrer for 24 h; at 75 °C ([C₄-py]Cl) or 85 °C ([C₆-py]Cl and [C₈-py]Cl). [C₄-py]Cl and [C₆-py]Cl, obtained in the form of the white solids directly after synthesis, were washed in Schlenk apparatus with diethyl ether (4×50 cm³) and hexane (4×50 cm³) and dried by nitrogen stream. [C₈-py]Cl obtained in the form of a transparent yellow, dense, and viscous liquid was cooled to room temperature and extracted by turns with diethyl ether (4×50 cm³) and hexane (4×50 cm³) and dried by nitrogen stream. Yields: 77% for [C₄-py]Cl, 39% for [C₆-py]Cl, and 52% for [C₈-py]Cl.

1-*n*-Butylpyridinium chloride, $[C_4$ -py]Cl: ¹³C NMR (400 MHz, CDCl₃ ppm) 13.58 (CH₃), 19.37 (CH₂), 34.01 (CH₂), 61.68 (NCH₂), 128.46 (2 ArC), 144.89 (1 ArC), 145.56 (2 ArC). ¹H NMR (400 MHz, CDCl₃ ppm) 0.91 (t, 3H), 1.38 (q, 2H), 2.01 (p, J=7.6 Hz, 2H), 5.02 (t, 2H), 7.89 (t, 2H), 8.47 (t, 1H), 9.75 (d, J=5.6 Hz, 2H). FT-IR (KBr, nujol) ν = 3012, 2949, 2935, 2871, 1628, 1488, 1170, 801, 698 cm⁻¹.

1-*n*-Hexylpyridinium chloride, [C₆-py]Cl: ¹³C NMR (400 MHz, CDCl₃ ppm) 13.27 (CH₃), 21.27 (CH₂), 24.99 (CH₂), 30.43 (CH₂), 31.38 (CH₂), 61.10 (NCH₂), 127.85 (1 ArC), 144.42 (2 ArC), 144.79 (2 ArC). ¹H NMR (400 MHz, CDCl₃ ppm) 0.53 (t, 3H), 1.01 (m, 6H), 1.78 (p, 2H), 4.74 (t, 2H), 7.92 (t, 2H), 8.21 (t, 1H), 9.51 (d, J=5.6 Hz, 2H). FT-IR (KBr) ν = 3022, 2958, 2930, 2859, 1633, 1487, 1172, 775, 687 cm⁻¹.

1-*n*-Octylpyridinium chloride, [C₈-py]Cl: ¹³C NMR (400 MHz, CDCl₃ ppm) 13.43 (CH₃), 21.90 (CH₂), 25.42 (CH₂), 28.36 (CH₂), 28.39 (CH₂),



Fig. 1. Densities of the studied ionic liquids.

31.00 (CH₂), 31.52 (CH₂), 61.21 (NCH₂), 127.91 (1 ArC), 144.39 (2 ArC), 144.87 (2 ArC). ¹H NMR (400 MHz, CDCl₃ ppm) 0.60 (t, 3H), 1.09 (m, 10H), 1.88 (p, 2H), 4.81 (t, 2H), 7.99 (t, 2H), 8.33 (t, 1H), 9.58 (d, J = 5.6 Hz, 2H). FT-IR (KBr) ν = 3013, 2956, 2927, 2856, 1635, 1489, 1172, 780, 691 cm⁻¹.

To the obtained 1-alkylpyridinium chlorides, the equimolar amount of aluminium chloride was added stepwise carefully under a nitrogen atmosphere at room temperature. The mixtures were magnetically stirred and the transparent, slightly brownish chloroaluminate ionic liquids were obtained.

$$1 - n - butyl - 4 - methylpyridinium tetrachloroaluminate,$$

$$[C_4 - 4 - mpy][AlCl_4]$$
(7)

$$1 - n - hexyl - 4 - methylpyridinium tetrachloroaluminate,$$
 (8)
 $[C_6 - 4 - mpy][AlCl_4]$

$$1 - n - \text{octyl} - 4 - \text{methylpyridinium tetrachloroaluminate},$$
(9)
$$[C_8 - 4 - \text{mpy}][\text{AlCl}_4]$$

4-Picoline (0.4 mol) and 1-chlorobutane (or 1-chlorohexane or 1chlorooctane) (0.4 mol) were placed into a 250 cm³ round bottom flask equipped with an electric heat-jacket and vigorously stirred using a magnetic stirrer at 75 °C for 72 h. In the case of the 1-nbutyl-4-methylpyridinium chloride, [C₄-4-mpy]Cl and 1-n-hexyl-4methylpyridinium chloride, [C₆-4-mpy]Cl the brownish solid forms were obtained directly after synthesis. The resulting solids were washed in Schlenk apparatus with diethyl ether $(4 \times 50 \text{ cm}^3)$ and hexane $(4 \times 50 \text{ cm}^3)$ and dried by nitrogen stream. In the case of 1-*n*-octyl-4methylpyridinium chloride, [C₈-4-mpy]Cl, a transparent, brownish, dense, and viscous liquid was obtained. It was cooled to room temperature and extracted by turns with diethyl ether $(4 \times 50 \text{ cm}^3)$ and hexane $(4 \times 50 \text{ cm}^3)$. After the hexane extraction, the residual liquid crystallized. The resulting solid was filtered off by means of Schlenk apparatus and dried by nitrogen stream. Yields: 39% for [C₄-4-mpy]Cl, 35% for [C₆-4mpy]Cl, and 52% for [C₈-4-mpy]Cl.

1-*n*-Butyl-4-methylpyridinium chloride, $[C_4$ -4-mpy]Cl: ¹³C NMR (400 MHz, CDCl₃ ppm) 13.12 (CH₃), 18.93 (CH₂), 21.80 (CH₂), 33.88 (CH₃), 60.50 (NCH₂), 128.37 (2 ArC), 144.07 (2 ArC), 158.15 (1 ArC). ¹H NMR (400 MHz, CDCl₃ ppm) 0.96 (t, *J*=7.2 Hz, 3H), 1.41 (sextet, *J*= 8.0 Hz, 2H), 2.01 (p, *J*=7.6 Hz, 2H), 2.67 (s, 3H), 4.96 (t, *J*=7.2 Hz, 2H), 7.89 (d, *J*=6.4 Hz, 2H), 9.48 (d, *J*=6.4 Hz, 2H). FT-IR (KBr, nujol) ν = 2991, 2955, 2931, 2860, 1642, 1522, 1468, 1173, 844 cm⁻¹.

1-*n*-Hexyl-4-methylpyridinium chloride, $[C_6-4$ -mpy]Cl: ¹³C NMR (400 MHz, CDCl₃ ppm) 13.50 (CH₃), 21.79 (CH₂), 21.93 (CH₂), 25.29 (CH₂), 30.73 (CH₂), 31.46 (CH₃), 60.73 (NCH₂), 128.40 (2 ArC), 144.04 (2 ArC), 158.15 (1 ArC). ¹H NMR (400 MHz, CDCl₃ ppm) 0.84 (t, *J* = 7.2 Hz, 3H), 1.31 (m, 6H), 2.01 (p, *J* = 7.4 Hz, 2H), 2.67 (s, 3H), 4.93 (t, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 6.4 Hz, 2H), 9.47 (d, *J* = 6.4 Hz, 2H). FT-IR (KBr, nujol) ν = 2991, 2955, 2931, 2860, 1642, 1522, 1468, 1173, 844 cm⁻¹.

1-*n*-Octyl-4-methylpyridinium chloride, $[C_8-4$ -mpy]Cl: ¹³C NMR (400 MHz, CDCl₃, ppm) 13.57 (CH₃), 21.73 (CH₂), 22.07 (CH₂), 25.61 (CH₂), 28.53 (CH₂), 28.57 (CH₂), 31.18 (CH₂), 31.47 (CH₃), 60.62 (NCH₂), 128.44 (2 ArC), 144.07 (2 ArC), 158.08 (1 ArC). ¹H NMR (400 MHz, CDCl₃, ppm) 0.87 (t, *J*=6.8 Hz, 3H), 1.30 (m, 10H), 2.01 (p, *J*=7.4 Hz, 2H), 2.68 (s, 3H), 4.93 (t, *J*=7.2 Hz, 2H), 7.95 (d, *J*=6.0 Hz, 2H), 9.54 (d, *J*=6.8 Hz, 2H). FT-IR (KBr) ν =3009, 2956, 2928, 2856, 1641, 1519, 1469, 1173, 832 cm⁻¹.

To the obtained 1-alkyl-4-methylpyridinium chlorides, the equimolar amount of aluminium chloride was added carefully stepwise under a nitrogen atmosphere at room temperature. The mixtures were magnetically stirred and the transparent, slightly brownish chloroaluminate ionic liquids were obtained.

$$1 - n - \text{Octyl} - 3 - \text{methylpyridinium tetrachloroaluminate},$$
 (10)
([C₈ - 3 - mpy][AlCl₄]

 $[C_8-3-mpy]$ [AlCl₄] was synthesized according to the procedure presented for $[C_8-4-mpy]$ [AlCl₄]. Yield: 35%.

Table 3	
Viscosities (mPa·s) of the studied ionic liqui	ds.

No	Ionic liquids	Т (К)										
		293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
1	[C ₄ -mim][AlCl ₄]	34.0	29.0	25.0	21.3	18.5	16.4	14.6	13.0	11.1	9.9	8.7
2	[C ₆ -mim][AlCl ₄]	68.0	56.3	47.3	40.1	33.9	30.3	26.7	22.9	19.8	17.3	15.3
3	[C ₈ -mim][AlCl ₄]	93.3	79.8	64.7	55.0	45.9	39.9	34.0	28.6	23.9	20.7	17.8
4	[C ₄ -py][AlCl ₄]	Solid	Solid	34.5	28.3	25.1	21.4	19.3	17.5	15.9	14.7	13.6
5	[C ₆ -py][AlCl ₄]	65.3	57.3	49.4	41.7	37.4	33.4	28.3	25.4	23.1	21.0	19.0
6	[C ₈ -py][AlCl ₄]	79.5	67.3	56.2	46.9	40.9	34.4	30.6	26.8	23.5	21.0	18.7
7	[C ₄ -4-mpy][AlCl ₄]	49.4	41.3	34.8	29.5	25.2	20.8	18.0	15.5	13.3	11.9	10.5
8	[C ₆ -4-mpy][AlCl ₄]	73.3	59.5	48.9	40.7	34.1	29.2	25.0	21.7	17.9	15.5	13.1
9	$[C_8-4-mpy][AlCl_4]$	118.4	99.0	84.0	68.7	55.5	46.8	39.5	33.5	27.6	23.9	21.0
10	[C ₈ -3-mpy][AlCl ₄]	182.0	147.6	126.6	108.4	91.7	77.3	63.7	55.3	47.1	40.6	35.5
11	[Bzl-mim][AlCl ₄]	Solid	Solid	Solid	Solid	Solid	45.1	37.0	32.1	28.1	25.2	22.7
12	[Ph-C ₂ -mim][AlCl ₄]	Solid	Solid	Solid	Solid	92.2	72.7	59.2	46.7	37.3	30.1	24.0
13	$[C_4-mim][AlCl_4]/[Ph-C_2-mim][AlCl_4] = 1/1$	92.4	74.8	60.6	50.1	41.7	36.4	32.1	28.1	26.0	23.5	21.6
14	$[C_4-mim][AlCl_4]/[Ph-C_2-mim][AlCl_4] = 1.5/1$	75.1	60.0	50.6	41.6	35.6	30.4	27.0	23.7	21.1	19.3	17.2
15	[C ₄ -mim][AlCl ₄]/AlCl ₃	30.8	27.0	24.1	21.0	18.4	16.4	14.8	13.5	12.1	11.0	9.9
	$\chi = 0.65$											
16	[C ₄ -mim][AlCl ₄]/AlCl ₃	31.4	27.3	23.7	20.8	18.3	16.4	14.7	13.3	12.0	10.8	9.8
	$\chi = 0.7$											
17	[C ₄ -mim][AlCl ₄]/hexane	32.4	27.8	24.0	21.0	18.5	16.4	14.5	13.0	-	-	-
18	[C ₄ -mim][AlCl ₄]/toluene	18.2	16.6	14.6	13.1	11.6	10.5	9.6	8.6	7.8	7.1	6.6
19	[C ₄ -py][AlCl ₄]/AlCl ₃	29.8	26.4	22.8	19.9	17.6	15.8	13.8	12.6	11.3	10.2	9.3
	$\chi = 0.65$											
20	[C ₄ -py][AlCl ₄]/AlCl ₃	29.0	25.2	22.1	19.9	17.6	15.6	14.2	12.9	11.7	10.7	9.6
	$\chi = 0.7$											
21	[C ₄ -py][AlCl ₄]/hexane	Solid	Solid	28.3	24.4	21.1	18.5	16.4	14.6	-	-	-
22	[C ₄ -py][AlCl ₄]/toluene	Solid	13.8	12.8	10.8	9.4	8.5	7.6	7.1	6.5	6.0	5.6

1-*n*-Octyl-3-methylpyridinium chloride, $[C_8$ -3-mpy]Cl: ¹³C NMR (400 MHz, CDCl₃, ppm) 14.43 (CH₃), 18.34 (CH₂), 22.52 (CH₂), 25.88 (CH₂), 28.82 (CH₂), 28.91 (CH₂), 31.12 (CH₂), 31.61 (CH₃), 61.03 (NCH₂), 127.80 (ArC), 139.22 (ArC), 142.48 (ArC), 144.73 (ArC), 146.19 (ArC). ¹H NMR (400 MHz, CDCl₃, ppm) 0.84 (t, J=6.8 Hz, 3H), 1.24 (m, 10H), 1.90 (p, 2H), 4.54 (t, 2H), 8.05 (q, J_1 =6.0 Hz, J_2 =2.0 Hz, 1H), 8.44 (d, J=8.0 Hz, 1H), 8.95 (d, J=6.0 Hz, 1H), 9.05 (s, 1H). FT-IR (KBr) ν =3015, 2955, 2927, 2855, 1634, 1505, 1467, 1155, 814, 689 cm⁻¹.

1 - Benzyl - 3 - methylimidazolium chloroaluminate,(11) [BzImim][AlCl₄]

Benzyl chloride (0.4 mol) was dropped into methylimidazole (0.4 mol), stirred at 40 °C. The mixture was stirred for 5 h at 70–110 °C. The obtained crude 1-benzyl-3-methylimidazolium chloride, [Bzlmim]Cl, in the form of a light-orange viscous oil was dissolved in 70 cm³ acetonitrile and washed with diethyl ether (3×40 cm³), ethyl acetate (4×20 cm³), and again with diethyl ether (4×50 cm³), and finally with hexane (4×50 cm³). The product was left to stand over the hexane phase overnight to crystallize. The solid form was dried by nitrogen flow in a Schlenk apparatus to reach a constant weight. The product was obtained in the form of an off-white powder with 78% yield.

¹H NMR (CDCl3) δ 10.84 (1H, s), 7.51 (1H, s), 7.49–7.47 (2H, m), 7.38–7.36 (4H, m), 5.59 (2H, s), 4.07 (3H, s); ¹³C NMR (CDCl₃) δ 138.1 (s), 133.2 (s), 129.5 (s), 129.4 (s), 129.0 (s), 123.6 (s), 121.8 (s), 53.3 (s), 36.7 (s). FT-IR (KBr, nujol) ν = 3136, 3062, 2853, 1571, 1456, 1162, 1083, 856, 723, 699, 623 cm⁻¹.

To the obtained [BzImim]Cl an equivalent amount of aluminium chloride was added slowly while the mixture was constantly stirred. The obtained 1-benzyl-3-methylimidazolium chloroaluminate, liquid during synthesis, crystallized in the form of an off-white solid.

1 - (2 - Phenylethyl) - 3 - methylimidazolium chloroaluminate, (12) [Ph - C₂mim][AlCl₄]

2-Chloroethylbenzene (0.4 mol) was dropped into methylimidazole (0.4 mol), stirred at 70 °C. The light-brown mixture was stirred for 1 h at 90 °C. The crude product, in the form of a light-brown viscous oil, was

cooled to room temperature and washed using 30 cm³ diethyl ether. [Ph-C₂mim]Cl, 1-(2-phenylethyl)-3-methylimidazolium chloride crystallized. It was further purified by diethyl ether (4×30 cm³) and hexane (4×50 cm³) in a Schlenk apparatus. The product obtained was in the form of an off-white powder with 80% yield.

¹H NMR 4 (CDCl₃) δ 10.62 (1H, s), 7.42 (1H, t, J = 1.8 Hz), 7.31–7.18 (6H, m), 4.63 (2H, t, J = 7.4 Hz), 4.04 (3H, s), 3.24 (2H, 7, J = 7.4 Hz); ¹³C NMR (CDCl₃) δ 138.2 (s), 135.9 (s), 129.0 (s), 128.9 (s), 127.5 (s), 123.0 (s), 122.3 (s), 51.1 (s), 36.6 (s), 36.6 (s). FT-IR (KBr, nujol) ν = 3141, 3061, 2857, 1572, 1455, 1167, 1084, 856, 755, 703, 622 cm⁻¹.

To the obtained [Ph- C_2 mim]Cl, an equivalent amount of aluminium chloride was added slowly while the mixture was stirred continually. The obtained 1-(2-phenylethyl)-3-methylimidazolium chloroaluminate, liquid during synthesis, crystallized in the form of a light-orange solid.

2.3. Apparatus and procedures

The purity of the ionic liquids was checked by NMR spectroscopy (Bruker Ultrashield spectrometer (400 MHz).

The FTIR analysis was accomplished using a Nicole Nexus 2002 FTIR spectrometer from 4000 to 400 cm⁻¹ with a 2 cm⁻¹ resolution. The FTIR analysis of the ionic liquids was investigated in Nujol KBr/KBr.

To date, researchers have treated ionic liquids as Newtonian fluids, and no data have so far been published to indicate that there are ionic liquids that are non-Newtonian [51]. Viscosities of the ionic liquids were determined using a Brookfield model Alpha L (FungiLab) equipped with a small sample adapter (APM), volume 8 cm³, with a thermostatic jacket, and temperature control accuracy of ± 0.2 °C. The viscometer was calibrated frequently according to the instructions using standard calibration fluids (Brookfield viscosity standard: fluid 100, viscosity 99.3 cP (mPa ·s) in 298.15 K and fluid 50, viscosity 48.4 cP (mPa s) in 298.15 K) provided by the supplier. The ionic liquid samples were analysed in a temperature range 293.15–328.15 K, in inert atmosphere (glove-box, nitrogen flow), using TL5-type spindle, at RPM = 50. Each measurement was repeated three times and the average values were calculated.

Densities were determined using a Gay-Lussac glass pycnometer with thermometer-in-glass, of nominal volumetric capacity 5.00 cm³.



Fig. 2. Viscosities of the studied ionic liquids.

Gay-Lussac bottle has ground-in, perforated glass stoppers with outer ground-on cap. The temperature was maintained using thermostatic bath with a precision of ± 0.01 K. Density measurements were realized

with an accuracy of at least ± 0.0001 g·cm⁻³. At all temperatures, the pycnometer was calibrated by ultra-pure water. All density measurements were repeated at least three times.

To determine the density and viscosity of the mixtures of the ionic liquids with toluene, 15 wt.% of toluene was applied, the mixture was mixed 1 h at given temperature in a closed vessel and then the measurements were performed. In the case of hexane similar procedure was applied, however, due to poor miscibility of hexane with the ionic liquids, the mixture was mixed 1 h at given temperature in a closed vessel and then, the lower phase was taken.

3. Results and discussion

3.1. Density

Density measurements were carried out at temperatures ranging from 293.15 to 328.15 K. Density data for few studied ionic liquids (Table 1, items 1, 15, and 19) are already available in the literature [15,52]. Presented experimental data are in good agreement with the available literature values at 298 K, relative deviations range from 0.5 to 1.0%. To the best of our knowledge, no literature data on densities were previously determined for other studied ionic liquids.

Analysis of the data presented in Table 2 and Fig. 1 reveals that the density decreases with the increase of the length of the alkyl chain, regardless of the kind of the cation (imidazolium 1–3, pyridinium 4–6, methylpyridinium 7-9) or even the aromatic function in the chain (11-12). This is in accordance with general trends observed for all ionic liquids; the density decreases as the size of the cation increases [51]. As expected, the density decreases with increase in temperature [8,53]. The type of cation also influences the ionic liquid density. However the order is different than for non-haloaluminate ionic liquids [8]. For the ionic liquids with *n*-butyl (1, 4, 7) and *n*-hexyl alkyl chain (2, 5, 8) the density decreases in the order: pyridinium>imidazolium> methylpyridinium. It is regardless of the temperature applied and can be explained by the cation size. However, for *n*-octyl alkyl chain (3, 6, **9**) the order is changed: pyridinium>methylpyridinium>imidazolium. The possible explanation is the nano-segregated structure of ionic liquids. The high-charge and low-charge density regions of the ions that compose ionic liquids tend to be segregated into a polar network and non-polar domains. The latter, depending on the relative size of the high-charge and low-charge regions in each ion, can exist as isolated (dispersed) islands or a second continuous phase. The percolation limit corresponding to the transition from a dispersed to a continuous non-polar phase can be attained with longer alkyl-side chains [54].

The molecular volumes drawn on the basis of the measured densities also increase with the increase of the alkyl chain as well as the measurement temperature. The average molar volume change varied from $28.7 \pm 0.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ (**5–6**) to $41.2 \pm 0.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ (**2–3**) by the addition of $-\text{CH}_2\text{CH}_2$ – group. The highest molecular volume change is observed for aralkyl ionic liquids (**11**, **12**) for which the value equals $29.6 \pm 0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$ for single methylene group ($-\text{CH}_2-$). Generally it is higher than those with shorter side chain (*n*-propyl, *n*-butyl) [55] and can be explained by greater disorder caused by longer alkyl chain.

The position of the alkyl chains at the ionic liquid cation also influences density. Comparison of 4-methylpirydinium (**9**) and 3-methylpyriddinium (**10**) ionic liquids shows that *meta* position increases density. Similar trend can be observed when compared imidazolium (**1–3**) and 4-methylpirydinium (**7–9**) ionic liquids, although the longer alkyl chain diminishes differences or even invert the order (**3**, **9**). This phenomenon can be observed e.g. in xylenes [56] and can be ascribed to molecular symmetry and packing. Interestingly, 1-*n*-octyl-3-methylpiridinium tetrachloroaluminate (**3**) has lower density than 1-*n*-octyl-3-methylpyridinium analog (**10**).

The aralkyl ionic liquids (**11**, **12**) have relatively higher densities and they are solid in major range of temperatures of the measurements. However, addition of commercial accessible 1-*n*-butyl-3-methylpyridinium

Table 4

Activation energies (E_{η}) for viscous flow and viscosity at infinite temperature (η_{∞}) for the studied ionic liquids.

No	Ionic liquid	E_{η} (kJ·mol ⁻¹)	$10^2 \cdot \eta_{\infty} (mPa \cdot s)$	r ²
1	$[C_4-mim][AlCl_4]$	22.50 (±1%)	0.33 (±1%)	0.9992
2	[C ₆ -mim][AlCl ₄]	24.61 (±1%)	$0.25(\pm 2\%)$	0.9990
3	[C ₈ -mim][AlCl ₄]	28.00 (±1%)	0.14 (±2%)	0.9993
4	[C ₄ -py][AlCl ₄]	19.71 (±4%)	$1.30(\pm 4\%)$	0.9873
5	[C ₆ -py][AlCl ₄]	20.95 (±2%)	1.20 (±2%)	0.9980
6	[C ₈ -py][AlCl ₄]	24.29 (±1%)	0.37 (±2%)	0.9985
7	$[C_4-4-mpy][AlCl_4]$	26.26 (±1%)	0.10 (±2%)	0.9993
8	$[C_6-4-mpy][AlCl_4]$	28.29 (±1%)	0.07 (±2%)	0.9993
9	$[C_8-4-mpy][AlCl_4]$	29.62 (±1%)	0.06 (±2%)	0.9991
10	[C ₈ -3-mpy][AlCl ₄]	27.42 (±1%)	0.24 (±2%)	0.9991
11	[Bzl-mim][AlCl ₄]	24.54 (±5%)	0.41 (±3%)	0.9903
12	[Ph-C ₂ -mim][AlCl ₄]	39.96 (±1%)	$2 \cdot 10^{-5} (\pm 1\%)$	0.9993
13	$[C_4-mim][AlCl_4]/[Ph-C_2-mim]$	24.28 (±4%)	0.41 (±6%)	0.9859
	$[AlCl_4] = 1/1$			
14	$[C_4-mim][AlCl_4]/[Ph-C_2-mim]$	24.36 (±3%)	0.32 (±4%)	0.9934
	$[AlCl_4] = 1.5/1$			
15	$[C_4-mim][AlCl_4]/AlCl_3, \chi = 0.65$	18.95 (±1%)	1.29 (±1%)	0.9994
16	$[C_4-mim][AlCl_4]/AlCl_3, \chi = 0.7$	19.35 (±1%)	1.10 (±1%)	0.9993
17	[C ₄ -mim][AlCl ₄]/hexane	20.82 (±1%)	0.63 (±1%)	0.9969
18	[C ₄ -mim][AlCl ₄]/toluene	17.34 (±1%)	1.50 (±1%)	0.9994
19	$[C_4-py][AlCl_4]/AlCl_3, \chi = 0.65$	19.65 (±1%)	0.94 (±1%)	0.9994
20	$[C_4-py][AlCl_4]/AlCl_3, \chi = 0.7$	18.21 (±1%)	1.63 (±1%)	0.9993
21	[C ₄ -py][AlCl ₄]/hexane	21.91 (±1%)	0.47 (±1%)	0.9992
22	[C ₄ -py][AlCl ₄]/toluene	17.51 (±3%)	1.17 (±3%)	0.9910

The percentage standard errors have been included.

tetrachloroaluminate (1) results in liquid mixture (13, 14) of average density of both constituents (13).

Increase of the effective molar fraction of AlCl₃ (χ) results in considerable increase of the density of the chloroaluminate ionic liquids (**1**, **15**, **16** and **4**, **19**, **20**), what is observed also in literature [15]. When χ equals 0.65, generally Al₂Cl₇⁻ anions are present. This enables comparison of the molecular volumes of the ionic liquids **1** and **15** as well as **4** and **19**, which increase with the effective molar fraction of AlCl₃ (247.9 (**1**), 333.56 (**15**), 238.8 (**4**), 322.7 (**19**) cm³ · mol⁻¹ at 301.15 K). The increase of the density of the ionic liquids having higher effective molar fraction of AlCl₃ shows that molecular weight of the chloroaluminate ionic liquids increase faster than effective anion size. This is in accordance with data for imidazolium non-haloaluminate ionic liquids where the density increases with increasing molecular weight of the anion [57].

In most applications, the ionic liquids are used in mixtures with other compounds. Density of two most commonly applied ionic liquids were investigated by addition of two solvents, aliphatic hexane (**17**, **21**) and aromatic toluene (**18**, **22**), in order to mimic an influence of organic phase in biphasic liquid-liquids processes. As can be seen, addition of even small volumes of the solvents considerably decreases the densities of these ionic liquids, regardless of the nature of the solvents. Even

Table 5

No	Ionic liquid	D (B/	A (mPa·s)	B (K)	T ₀ (K)
		T ₀)			
4	[C ₄ -py][AlCl ₄]	0.54	3.6 (±2%)	132 (±1%)	244 (±1%)
5	[C ₆ -py][AlCl ₄]	3.86	0.7 (±5%)	613 (±1%)	162 (±1%)
6	[C ₈ -py][AlCl ₄]	5.17	0.4 (±3%)	710 (±1%)	153 (±1%)
11	[Bzl-mim][AlCl4]	0.35	6.2 (±2%)	96 (±1%)	268 (±1%)
13	$[C_4-mim][AlCl_4]/[Ph-C_2-mim]$	0.68	4.5 (±3%)	162 (±1%)	240 (±1%)
	$[AlCl_4] = 1/1$				
14	$[C_4-mim][AlCl_4]/[Ph-C_2-mim]$	1.21	1.8 (±2%)	289 (±1%)	218 (±1%)
	$[AlCl_4] = 1.5/1$				
17	[C ₄ -mim][AlCl ₄]/hexane	2.43	0.7 (±2%)	437 (±1%)	178 (±1%)
18	[C4-mim][AlCl4]/toluene	20.73	0.1 (±5%)	1327 (±1%)	63 (±2%)
21	[C ₄ -py][AlCl ₄]/hexane	3.28	0.4 (±1%)	558 (±1%)	173 (±1%)
22	[C ₄ -py][AlCl ₄]/toluene	0.52	$1.7 (\pm 5\%)$	125 (±3%)	242 (±1%)

The percentage standard errors have been included.

aliphatic solvent as hexane, considered immiscible with ionic liquid, influences density. Aromatic solvent as toluene, partially miscible with the ionic liquids influences density to greater extend. Nevertheless, the density order is preserved; *n*-butylpyridinium chloroaluminate has higher density (**21**, **22**) than imidazolium analog (**17**, **18**) which enables to assume that similar effect occurs in other ionic liquids.

3.2. Viscosity

Table 3 and Fig. 2 present the viscosity of the studied ionic liquids at temperatures ranging from 293.15 to 343.15 K. Single point comparison for [C₄-mim][AlCl₄] (1) at 298.15 K shows relative deviation 7.5%, whereas for the effective molar fraction of AlCl₃ χ = 0.65 ([C₄-mim][Al₂Cl₇] (15) and [C₄-py][Al₂Cl₇] (19)) deviation equals 11% and 20%, respectively. It should be noted, that the presented values are higher than literature data. The most probable reason of differences is water content; the higher water content the lower viscosity measured, [11]. Studies at non-haloaluminate alkylimidazolium ionic liquids revealed that relative-ly small amounts of impurities can have considerable impact on the ionic liquid viscosity [49,58].

As expected, the viscosities of the studied ionic liquids decrease with increase in temperature, which was reported for non-haluminate ionic liquids [8,53]. Nevertheless, this decrease is considerable greater than for densities. In the studied range of temperatures (293.15–343.15 K), within the intercept of 50 K, the average change of the values viscosity at 328.15 K diminish roughly 70% when compared to the values at 293.15 K. Generally, the longer the alkyl chain is the greater change in viscosity.

Structure of the organic cation has an influence on viscosity of the ionic liquid [9-11,14,59,60]. For the studied neutral 1-n-alkyl-3methylimidazolium (1-3), 1-n-alkylpyridinium (4-6), and 1-n-alkyl-4methylpyridinium (7-9) chloroaluminates viscosity increases with increasing length of the alkyl chain at the cation. Literature reports indicate molar mass effects, van der Waals interactions, chain tangling and hydrogen bonding interactions as main factors influencing viscosity [9,10,14,59]. It seems that lower viscosity values at shorter alkyl chain combine reduced side chain mobility and low molecular mass [59]. Alkyl chain lengthening makes the ionic liquids more viscous, due to increased van der Waals interactions. However, it is not a linear trend. For imidazolium (1-3) and pyridinium (4-6) ionic liquids the increase of the length of the alkyl chain from C4 to C6 results in grater change of the viscosity than from C6 to C8. For methylpyridinium analogs (7–9) the order is reversed; the increase of the length of the alkyl chain from C4 to C6 results in smaller change of the viscosity than from C6 to C8. The position of the alkyl chain also influences viscosity. This can be seen when compared isomers (9 and 10), where the isomer meta is considerably more viscous than the isomer para.

Replacement of the 1-alkyl group with 1-aralkyl unit (**11**, **12**) increases viscosity when compared to alkyl analog having similar number of carbon atoms at the side chain (**3**, **12**). This can be probably due to π -stacking of the benzene rings at the side chains of neighbouring molecules. However, the measurement of the aralkyl ionic liquids is limited at lower temperatures due to their tendency to crystallize. Relatively high viscosity of the aralkyl ionic liquids and solid state at lower temperatures limit their broader applications. This can be overcome by mixing them with other ionic liquids (**13**, **14**). As can be seen, the viscosity decreases with the increase of the amount of less viscous constituent of the mixture and is roughly twice smaller as compared to pure aralkyl ionic liquid.

The presence of common solvents decreases the viscosity of the ionic liquid [61–64]. We determined the viscosity of two ionic liquids (**1**, **5**) with the presence of aliphatic hexane (**17**, **21**) and aromatic toluene (**18**, **22**). Evaporation of volatile hexane at higher temperatures influences the measurement error, and thus not all the studied ranges of temperatures were presented. Nevertheless, the results indicate that hexane (**17**, **21**) reduces the viscosity at most 5% for **17** and 18% for

21. It means that aliphatic solvent has relatively small influence on the viscosity of the ionic liquid, which can be important information for those who apply the ionic liquids in biphasic liquid-liquid processes. Greater changes are observed in the case of toluene (**18**, **22**). Addition of 15 wt.% reduces the viscosity of the ionic liquids twice (56–61% for **18**, and 43–47% for **22**). Viscosities of the mixtures with these solvents decrease with the increase of temperature.

Increase of the effective molar fraction of AlCl₃ (χ) results in decrease of the viscosity of the chloroaluminate ionic liquids (**15**, **16** and **19**, **20**). Similar results were obtained for 1-ethyl-3-methylimidazolium chloroaluminates at single 298 K [15]. The presented data reveal that this effect diminishes at higher temperatures. For the imidazolium ionic liquid (**15**, **16**) the viscosity is reduced about at most 14% at 293.15 K whereas from 318.15 K the effect can be neglected. For the pyridinium ionic liquid (**19**, **20**) the mixtures are liquid and the viscosity is reduced about 1/3 in the range 303.15–343.15 K. The observed decrease of the haloaluminate ionic liquid viscosities with the increase of the effective molar fraction of AlCl₃ may be explained by decreased ion interaction due to lower symmetry and improved charge distribution. For non-haloaluminate ionic liquids decrease of viscosity with increase of anion size can be observed when compared [CF₃BF₄⁻] to [C₂F₅BF₄⁻] anions, but not for analogs with longer perfluorinated alkyl chain [65].

Instead of the analysis of the absolute viscosities presented in Table 3, another approach uses the plot of dependence viscosity from temperature. If linear, as in the case of majority of the studied ionic liquids, it is fitted with the logarithmic form of Arrhenius Eq. (1).

$$\ln \eta = \ln \eta_{\infty} + E_{\eta} / RT \tag{1}$$

From the slope and intercept of the Arrhenius plot the activation energy for viscous flow (E_{η}) and the viscosity at infinite temperature (η_{∞}) were determined, respectively. The activation energy for viscous flow $(E_{\rm m})$ equals energy barrier, which must be overcome in order for the ions to move past each other in the ionic liquid. Thus, the E_{η} values correlate with structure of the studied ionic liquids. The higher E_{η} value the more difficult for the ions to move past each other. This can results of the physical size of the ions or their entanglement with neighbouring ions by changing the number or strength of interactions. The infinite temperature (η_{∞}) is temperature where interactions amongst the ions do not influence the viscosity of the ionic liquid and this viscosity is determined only by geometric structure of the ions. It enables to attain information about dependence between the structure of the cation and the viscosity of the ionic liquid [14]. Table 4 presents the activation energy (E_n) and viscosity at infinite temperature (η_{∞}) for the studied ionic liquids.

As can be seen, the E_{η} values increase with increase of the length of the side chain at the ionic liquid cation as well as by incorporation of the aromatic functional group. It is also increases in the order of cation: pyridinium<imidazolium<methylpyridinium. This results from an increase of the van der Waals interactions, higher molecular mass, as well as ring-stacking in the case of aralkyl side chain. In contrast, the η_{∞} values decrease with increase of the length of the side chain (1–9, 11, 12), which indicates that the longer alkyl chain the more difficult for the ions to move past each other. Comparison of *para* and *meta* analogs (9, 10) indicates that that ions of smaller symmetry move past each other more difficult. Additions, such as co-solvents or AlCl₃, decrease the E_{η} values. The result is in agreement with the trends described in by absolute viscosities (Table 3).

It should be noted, however, that not all studied ionic liquids fitted well to Arrhenius model at the studied temperature range ($r^2 > 0.999$). Particularly this concerns the mixed ionic liquids and those with organic co-solvent. Although, for **18** and **21** the Arrhenius model still is valid in the studied temperature range, a curvature in the temperature dependence plots can be seen. Interestingly, the pyridinium (**4–6**) and benzylimidazolium (**11**) ionic liquids poorly fit to the Arrhenius model, which probably can be connected to their particular tendency to

crystallise at lower temperatures. For the ionic liquids having non-Arrhenius viscosity temperature dependence, Eq. (2) proposed by Vogel–Fulcher–Tammann (VFT) was applied [53,66],

$$\ln \eta = \ln A + B/(T - T_0) \tag{2}$$

where T is the absolute temperature, and A, B, and T_0 are adjustable parameters (Table 5). As can be seen, the Angel strength parameter D (\equiv B/T₀) is greater for those ionic liquids, for which the viscosity approaches an Arrhenius temperature dependence [66]. The B value increases with decreasing A and T₀ values, which is also reported for other ionic liquids [14,53]. The glass temperature T₀ is the highest for the aralkyl ionic liquid (**11**). It decreases with increase of the length of the alkyl chain at the ionic liquid cation (**4–6**) as well as with increase of the anion size (**13**, **14**). It is interesting to compare different changes the parameters for the imidazolium and pyridinium ionic liquids with the presence of organic solvents. For the imidazolium ionic liquid (**18**) the value of the parameter B is considerably large and the glass temperature T₀ is relatively small in the presence of aromatic toluene. In contrast, for the pyridinium analogs the values of these parameters remain generally unchanged.

4. Conclusion

The chloroaluminate ionic liquids have not been previously investigated very extensively. We have presented densities and viscosities for series of various chloroaluminate ionic liquids, based on most common imidazolium and pyridinium cations. The influence of the side chain at the cation (type, length, and position), amount of AlCl₃ (anion effect), presence of typical organic solvent (aromatic toluene, aliphatic hexane), and mixing of different ionic liquids was studied. The density and viscosity were measured in the range of temperatures (298.15-328.15 K) and (298.15–343.15 K), most commonly applied in various reactions where the ionic liquids are used as reaction media, in which transition metal catalysts are often immobilized. Our laboratory practice indicates that decrease of the ionic liquid density and increase of the viscosity makes more difficult to separate the ionic liquid phase form other immiscible phase or reaction products. On the other hand, this often results in higher reaction yield, because more viscous and less dense ionic liquid medium increases dispersity of the system an thus enables more efficient contact of the reagents as well as access to the catalyst active sites.

The changes of density and viscosity of the studied chloroaluminate ionic liquids are often similar to those for non-haloaluminate analogs. However, there are some differences, like in the case of the cation order in the case of density. The influence of the longer alkyl chain (hexyl and octyl) at the ionic liquid cation is worth to notice. It is shown that the mixing of the ionic liquid enable not only to tailor their physical properties as reaction medium, but also prevent their crystallization to solid form. This broadens the temperature range of their application.

We believe that one can find the presented results valuable to rationalize the proper choice of the ionic liquid and thus to obtain better performance of the designed reactions in common laboratory work.

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